



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification<sup>6</sup> :</b> <b>B01J 29/04, 29/06, 21/00, 23/40, 23/58, 23/44, 23/42, 23/02, 23/20, 23/00, C04B 35/48, 35/03, 35/20, H01M 4/86, 8/08, G01N 27/26</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 98/55227</b>  <b>(43) International Publication Date:</b> 10 December 1998 (10.12.98)
<b>(21) International Application Number:</b> PCT/US98/10523  <b>(22) International Filing Date:</b> 22 May 1998 (22.05.98)  <b>(30) Priority Data:</b> 08/867,556                      2 June 1997 (02.06.97)                      US  <b>(71) Applicant:</b> THE UNIVERSITY OF CHICAGO [US/US]; 5801 South Ellis Street, Chicago, IL 60637 (US).  <b>(72) Inventors:</b> KRUMPELT, Michael; 12 S. 019 Book Road, Naperville, IL 60565 (US). AHMED, Shabbir; 101 Wedgewood Way, Bolingbrook, IL 60440 (US). KUMAR, Romesh; 1549 Ceals Court, Naperville, IL 60565 (US). DOSHI, Rajiv; 6871 Parker 6, Downers Grove, IL 60516 (US).  <b>(74) Agent:</b> LEVY, Harry, M.; Suite 3000, 300 South Wacker Drive, Chicago, IL 60606 (US).		<b>(81) Designated States:</b> CA, JP, RU, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i> <i>With amended claims and statement.</i>
<b>(54) Title:</b> PARTIAL OXIDATION CATALYST  <b>(57) Abstract</b>  <p>A two-part catalyst comprising a dehydrogenation portion and an oxide-ion conducting portion. The dehydrogenation portion is a group VIII metal and the oxide-ion conducting portion is selected from a ceramic oxide crystallizing in the fluorite or perovskite structure. There is also disclosed a method of forming a hydrogen rich gas from a source of hydrocarbon fuel in which the hydrocarbon fuel contacts a two-part catalyst comprising a dehydrogenation portion and an oxide-ion conducting portion at a temperature not less than about 400 °C for a time sufficient to generate the hydrogen rich gas while maintaining CO content less than about 5 volume percent. There is also disclosed a method of forming partially oxidized hydrocarbons from ethanes in which ethane gas contacts a two-part catalyst comprising a dehydrogenation portion and an oxide-ion conducting portion for a time and at a temperature sufficient to form an oxide.</p>		

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## PARTIAL OXIDATION CATALYST

**CONTRACTUAL ORIGIN OF THE INVENTION**

The United States Government has rights in this invention pursuant to Contract No. W-31-109-ENG-38 between the U.S. Department of Energy (DOE) and The University of Chicago representing Argonne National Laboratory.

**Background Of The Invention**

Fuel cell-powered vehicles are being developed by the domestic and foreign automotive industry as a more fuel efficient and less polluting alternative to the current internal combustion engines. Since the fuel cells operate preferably on hydrogen, but storing of hydrogen on-board a vehicle is not as convenient as carrying liquid hydrocarbon fuel in a tank, a "fuel processor" must generate the hydrogen.

Converting hydrocarbon fuels to hydrogen can be done by steam reforming (reaction of the hydrocarbon with steam) or by partial oxidation (reaction with a substoichiometric amount of air). Steam reforming reactors are fairly bulky and are heat-transfer limited. Partial oxidation is more rapid but less developed. See U.S. patent no. 5,248,566 issued September 28, 1993 to Kumar et al., the disclosure of which is incorporated by reference, for a general discussion of the use of a fuel cell in a vehicle.

It is highly desirable to provide a catalyst for the partial oxidation reaction so that the temperature, can be lowered from the 1000°C temperatures required for steam reformers. At lower temperatures, the reactors can be smaller, and the product gas contains higher concentrations of hydrogen and less carbon monoxide, which is desirable. However, an appropriate catalyst has heretofore not been available. This invention relates to a new family of catalysts that are effective for the conversion of a wide range of hydrocarbons, including aliphatic hydrocarbons to hydrogen.

**Summary of the Invention**

This invention relates to a partial oxidation catalyst. More specifically, this invention relates to a catalyst for partially oxidizing hydrocarbon fuels such as gasoline to produce a high percentage yield of hydrogen suitable for supplying a fuel cell. The difficulty of converting hydrocarbons (e.g. n-octane, iso-octane, etc.), a main component of gasoline, to hydrogen is the fact that the hydrogen/oxygen

bond is thermodynamically stronger than the carbon oxygen bond at moderate temperatures. Under thermal equilibrium conditions, the reaction products will therefore be rich in water and poor in hydrogen. In order to produce a hydrogen-rich gas, a bifunctional catalyst is required which can "dehydrogenate" the hydrocarbon molecule, and then selectively oxidize the carbon chain.

In one aspect of the invention, the catalyst is a cermet containing ceria as the oxide ion conduction material, and platinum as the hydrogen dissolving material. The catalyst can be prepared from a high surface area powder of doped ceria ( $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ ) and a second phase powder which could be either a metal  
10 like platinum or an oxide like  $\text{Co}_2\text{O}_3$  which is reduced in-situ in the reactor to cobalt metal. Other metals include all noble and transition metals. Other oxide ion conducting materials such as zirconia, bismuth oxides or vanadates, lanthanum gallate, perovskite containing manganese, iron, cobalt, or others forming oxygen deficient structures are applicable.

In another aspect of the invention, various alkanes can be oxidized by contact with the catalyst of the present invention to form alkene oxides, ketones or aldehydes.

### Brief Description of the Drawings

The invention consists of certain novel features and a combination of  
20 parts hereinafter fully described, illustrated in the accompanying drawings, and particularly pointed out in the appended claims, it being understood that various changes in the details may be made without departing from the spirit, or sacrificing any of the advantages of the present invention.

FIGURE 1 is a graph depicting the relationship between temperature and product gas composition for regular gasoline and a catalyst of Pt/CeGdO.

FIG. 2 is a graph depicting the relationship between temperature and product gas composition for premium gasoline and a catalyst of Pt/CeGdO.

FIG. 3 is a graph depicting the relationship between temperature and product gas composition for premium gasoline and a catalyst of Pt/CeSmLiO.

30 FIG. 4 is a graph depicting the relationship between temperature and product gas composition for natural gas and a catalyst of Pt/CeGdO.

### Detailed Description of the Invention

The difficulty of converting hydrocarbons such as n-octane (the main component of gasoline) to hydrogen is the fact that the hydrogen/oxygen bond is thermodynamically stronger than the carbon oxygen bond at moderate temperatures. Under thermal equilibrium conditions, the reaction product will therefore be rich in water and poor in hydrogen. We discovered that in order to get a hydrogen-rich gas one would have to find a catalyst that can "dehydrogenate" the hydrocarbon molecule, and then selectively oxidize the carbon chain. Thus, the catalyst must be bifunctional.

10           To dehydrogenate a hydrocarbon molecule, one can use metals that dissolve hydrogen such as platinum, nickel or any Group VIII metal. Ni is the least preferred because an oxidation product thereof,  $\text{NiO}_4$ , is poisonous. To selectively oxidize the carbon chain, we found that one is able to use a source of ionic oxygen. Ionic oxygen apparently reacts with the double bonds of a dehydrogenated hydrocarbon to form oxygen carbon bonds. Sources of ionic oxygen are oxides crystallizing in the fluorite or perovskite structure, such as for instance by way of example without limitation,  $\text{ZrO}_2$ ,  $\text{CeO}_2$ ,  $\text{Bi}_2\text{O}_3$ ,  $\text{BiVO}_4$ ,  $\text{LaGaO}_3$ . By combining such oxides with a hydrogen dissolving metal and passing a hydrocarbon/air mixture over it, we discovered it is possible to obtain hydrogen-rich  
20           gas from an aliphatic as well as aromatic hydrocarbons.

We chose for purposes of examples, only, ceria as the oxide ion conducting material, and platinum as the hydrogen dissolving metal. A cermet containing the catalysts were prepared by a solid state method. The starting powders were a high surface area (about  $32 \text{ m}^2/\text{gm}$ ) doped ceria ( $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ ) and a second phase. The starting second phase powder was either a metal like Pt or an oxide like  $\text{Co}_2\text{O}_3$  which is reduced in-situ in the reactor to cobalt metal.

The two powders were mixed in the desired ratios of 1% pt metal and 99 % ceramic along with some isopropyl alcohol and up to 5 wt% of a dispersing agent for the second phase (oleic acid for metals and Hypermer Kd2 from ICI  
30           Americas Inc. for oxides) and then milled vigorously in a high density polyethylene bottle with Tosoh milling media. The mixture was then dried to remove the alcohol while stirring on a hot plate to about  $70^\circ\text{C}$ , pressed into 1.125-1.5" pellets with

about 3 gms of powder using 10,000 to 12,000 lbs. load and fired at 1000°C for 15-60 mins. in air. The resulting pellet had a uniform pore structure to allow gas access.

Such catalysts were tested in a reactor with feed streams of a hydrocarbon fuel ( $C_nH_m$ ), water and oxygen. The liquid fuel and liquid water were vaporized in a heated coil under a temperature bath maintained at 130-140°C. Oxygen was mixed in with the vapors and the reactant mixture was then fed into the reactor tube. The three feeds were mixed such that the (oxygen/fuel) molar ratio was less than or equal to  $n/2$ , while the water/fuel (molar) ratio was greater than or equal to  $n$ . The feed rates were adjusted to obtain a residence time of between 0.1-2 second in contact with the catalysts.

The catalysts particles were packed inside the reactor, typically weighing 1.5-2.5 g and occupying 1-3  $cm^3$  of space. The reactor tube was kept in an electrically heated furnace and maintained at the desired temperature (200-700°C). Thermocouples located above and below the catalyst measured the temperature at the catalyst bed inlet and outlet, respectively.

Referring to Fig. 1, there is reported the results of tests using a Pt/CeGdO two part catalyst with regular gasoline. Fig. 2 shows the results of tests using a Pt/Ce GdO two part catalyst with premium gasoline. Fig. 3 shows the results of tests using a Pt/Ce Sm LiO two part catalyst with premium gasoline and Fig. 4 shows the results of Pt/CeGdO two part catalyst on natural gas.

In general, any Group VIII metal (or mixtures thereof) may be used in combination with an oxide-ion conducting ceramic crystallizing in the fluorite or perovskite structure. The oxide may be doped with a suitable rare earth, such as Gd or Sm or additionally with a suitable alkali or alkaline earth metal, such as Li or Na.

In general, the reaction, which is exothermic, should be conducted in the range of from about 400°C to about 900°C and preferably from about 500°C to about 750°C. The lower the temperature while maintaining high  $H_2$  concentration and low CO concentration, the better. It is important to obtain as high a concentration of hydrogen as possible, but one limiting aspect is the amount of CO found, which should preferably not exceed 5% by volume.

In another aspect of the invention, various alkanes, such as ethane, can be contacted with the inventive catalysts to form various oxides, such as ethylene oxide, ketones and aldehydes. The reaction has to be at a temperature and for a time sufficient to form the desired products, all parameters of time and temperature are within the skill of art.

While there has been disclosed what is considered to be the preferred embodiment of the present invention, it is understood that various changes in the details may be made without departing from the spirit, or sacrificing any of the advantages of the present invention.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A two-part catalyst comprising a dehydrogenation portion and an oxide -ion conducting portion.
2. The catalyst of claim 1, wherein the dehydrogenation portion includes a group VIII metal.
3. The catalyst of claim 1, wherein the dehydrogenation portion is selected from Pt, Pd and mixtures thereof.
4. The catalyst of claim 1, wherein the dehydrogenation portion  
10 includes a group VIII metal other than Ni.
5. The catalyst of claim 4, wherein the oxide-ion conducting portion is a ceramic oxide doped with an acceptable rare earth.
6. The catalyst of claim 5, wherein the ceramic oxide is doped with Gd, Sm or mixtures thereof and an acceptable alkali or alkaline earth metal.
7. The catalyst of claim 1, wherein the oxide-ion conducting portion is a ceramic oxide selected from the group consisting of  $\text{ZrO}_2$ ,  $\text{CeO}_2$ ,  $\text{Bi}_2\text{O}_3$ ,  $(\text{BiVO})_4$ ,  $\text{LaGaO}_3$  and mixtures thereof.
8. The catalyst of claim 7, wherein said two-part catalyst is effective  
20 at temperatures greater than about  $400^\circ\text{C}$  to produce a hydrogen-rich gas from a hydrocarbon fuel in contact therewith wherein the CO content is not greater than about 5% by volume.
9. The catalyst of claim 7, wherein said two-part catalyst is effective at temperatures between about  $500^\circ\text{C}$  and about  $900^\circ\text{C}$  to produce a hydrogen-rich gas from a hydrocarbon fuel in contact therewith having a CO content not greater than about 5% by volume.
10. The catalyst of claim 7, wherein said two-part catalyst is effective  
30 at temperatures in the range of from about  $500^\circ\text{C}$  to about  $900^\circ\text{C}$  to produce a hydrogen-rich gas from a hydrocarbon fuel in contact therewith, said hydrocarbon fuel being selected from gasoline, natural gas, gas rich in alkanes, gas containing branched alkanes and alkanes.
11. A two-part catalyst comprising a dehydrogenation portion selected from group VIII metals and mixtures thereof, and an oxide -ion conducting portion.



12. The catalyst of claim 11, wherein Ni is excluded.
13. The catalyst of claim 11, wherein the group VIII metal is Pt, Pd or mixtures thereof.
14. The catalyst of claim 12, wherein the oxide-ion conducting portion includes a ceramic.
15. The catalyst of claim 14, wherein the ceramic includes one or more of  $\text{ZrO}_2$ ,  $\text{CeO}_2$ ,  $\text{Bi}_2\text{O}_3$ ,  $(\text{BiVO})_4\text{O}_3$ ,  $\text{LaGaO}_3$ .
16. The catalyst of claim 15, wherein the ceramic is doped with a rare earth metal.
- 10 17. The catalyst of claim 16, wherein the rare earth metal doped ceramic is also doped with an alkali metal or an alkaline earth metal.
18. The catalyst of claim 13, wherein the group VIII metal is Pt and the oxide-ion conducting portion includes  $\text{CeO}_2$ .
19. The catalyst of claim 18, wherein the  $\text{CeO}_2$  is doped with a rare earth metal.
20. The catalyst of claim 19, wherein the  $\text{CeO}_2$  doped catalyst is  $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ .
21. The catalyst of claim 11, wherein the group VIII metal is Pd.
22. The catalyst of claim 21, wherein the oxide-ion conducting portion  
20 includes a ceramic including one or more of  $\text{ZrO}_2$ ,  $\text{CeO}_2$ ,  $\text{Bi}_2\text{O}_3$ ,  $(\text{V}+\text{Bi})_2\text{O}_3$  and  $\text{LaGaO}_3$ .
23. A two-part catalyst comprising a dehydrogenation portion and an oxide-ion conducting portion selected from a ceramic oxide crystallizing in the fluorite or perovskite structure.
24. The catalyst of claim 23, wherein said oxide-ion conducting ceramic is one or more of  $\text{ZrO}_2$ ,  $\text{CeO}_2$ ,  $\text{Bi}_2\text{O}_3$ ,  $(\text{BiVO})_4$ , and  $\text{LaGaO}_3$ .
25. A method of forming a hydrogen rich gas from a source of hydrocarbon fuel, comprising contacting the hydrocarbon fuel with a two-part catalyst comprising a dehydrogenation portion and an oxide-ion conducting portion  
30 at a temperature not less than about  $400^\circ\text{C}$  for a time sufficient to generate the hydrogen rich gas while maintaining the CO content less than about 5 volume percent.

26. The method of claim 25, wherein the hydrocarbon fuel is natural gas.

27. The method of claim 25, wherein the hydrocarbon fuel is gasoline.

28. The method of claim 25, wherein the hydrocarbon fuel includes alkanes.

29. The method of claim 28, wherein the hydrocarbon fuel also includes aromatics.

30. The method of claim 29, wherein the hydrocarbon fuel includes branched alkanes and alkenes.

10 31. The method of claim 26, wherein the dehydrogenation portion includes a group VIII metal, and the oxide-ion conducting portion is selected from a ceramic oxide from the group crystallizing in the fluorite or perovskite structure and mixtures thereof.

32. A method of forming partially oxidized hydrocarbons from ethanes comprising contacting ethane gas with a two-part catalyst comprising a dehydrogenation portion and an oxide-ion conducting portion for a time and at a temperature sufficient to form an oxide.

33. The method of claim 32, wherein the fuel is ethane and the product is ethylene oxide.

20 34. The method of claim 32, wherein the fuel is an alkane and the product is a ketone or aldehyde or mixtures thereof.

**AMENDED CLAIMS**

[received by the International Bureau on 16 November 1998 (16.11.98);  
original claims 16,17 and 32-34 cancelled; original claims 5-7,15,22-24 and 31  
amended; remaining claims unchanged (3 pages)]

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A two-part catalyst comprising a dehydrogenation portion and an oxide -ion conducting portion.
2. The catalyst of claim 1, wherein the dehydrogenation portion includes a group VIII metal.
3. The catalyst of claim 1, wherein the dehydrogenation portion is selected from Pt, Pd and mixtures thereof.
4. The catalyst of claim 1, wherein the dehydrogenation portion includes a group VIII metal other than Ni.
5. The catalyst of claim 4, wherein the oxide-ion conducting portion is a ceramic oxide doped a rare earth.
6. The catalyst of claim 5, wherein the ceramic oxide is doped with Gd, Sm or mixtures thereof and an alkali or alkaline earth metal.
7. The catalyst of claim 1, wherein the oxide-ion conducting portion includes a ceramic oxide selected from the group consisting of  $ZrO_2$ ,  $CeO_2$ ,  $Bi_2O_3$ ,  $(BiVO)_4$ ,  $LaGaO_3$  and mixtures thereof and a dopant selected from rare earths, the alkaline earth and alkali metals.
8. The catalyst of claim 7, wherein said two-part catalyst is effective at temperatures greater than about 400°C to produce a hydrogen-rich gas from a hydrocarbon fuel in contact therewith wherein the CO content is not greater than about 5% by volume.
9. The catalyst of claim 7, wherein said two-part catalyst is effective at temperatures between about 500°C and about 900°C to produce a hydrogen-rich gas from a hydrocarbon fuel in contact therewith having a CO content not greater than about 5% by volume.
10. The catalyst of claim 7, wherein said two-part catalyst is effective at temperatures in the range of from about 500°C to about 900°C to produce a hydrogen-rich gas from a hydrocarbon fuel in contact therewith, said hydrocarbon fuel being selected from gasoline, natural gas, gas rich in alkanes, gas containing branched alkanes and alkanes.

11. A two-part catalyst comprising a dehydrogenation portion selected from group VIII metals and mixtures thereof, and an oxide-ion conducting portion.

12. The catalyst of claim 11, wherein Ni is excluded.

13. The catalyst of claim 11, wherein the group VIII metal is Pt, Pd or mixtures thereof.

14. The catalyst of claim 12, wherein the oxide-ion conducting portion includes a ceramic.

15. The catalyst of claim 14, wherein the ceramic includes one or more of  $\text{ZrO}_2$ ,  $\text{CeO}_2$ ,  $\text{Bi}_2\text{O}_3$ ,  $(\text{BiVO})_4\text{O}_3$ ,  $\text{LaGaO}_3$  and a dopant selected from rare earths, the alkaline earth and alkali metals.

Cancel claim 16.

Cancel claim 17.

18. The catalyst of claim 13, wherein the group VIII metal is Pt and the oxide-ion conducting portion includes  $\text{CeO}_2$ .

19. The catalyst of claim 18, wherein the  $\text{CeO}_2$  is doped with a rare earth metal.

20. The catalyst of claim 19, wherein the  $\text{CeO}_2$  doped catalyst is  $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ .

21. The catalyst of claim 11, wherein the group VIII metal is Pd.

22. The catalyst of claim 21, wherein the oxide-ion conducting portion includes a ceramic including one or more of  $\text{ZrO}_2$ ,  $\text{CeO}_2$ ,  $\text{Bi}_2\text{O}_3$ ,  $(\text{V}+\text{Bi})_2\text{O}_3$  and  $\text{LaGaO}_3$  and a dopant selected from rare earths, the alkaline earth and alkali metals.

23. A two-part catalyst comprising a dehydrogenation portion and an oxide-ion conducting portion selected from a ceramic oxide crystallizing in the fluorite structure or  $\text{LaGaO}_3$ .

24. The catalyst of claim 23, wherein said oxide-ion conducting ceramic is one or more of  $\text{ZrO}_2$ ,  $\text{CeO}_2$ ,  $\text{Bi}_2\text{O}_3$ ,  $(\text{BiVO})_4$  and a dopant selected from rare earths, the alkaline earth and alkali metals.

25. A method of forming a hydrogen rich gas from a source of hydrocarbon fuel, comprising contacting the hydrocarbon fuel with a two-part catalyst comprising a dehydrogenation portion and an oxide-ion conducting portion

at a temperature not less than about 400°C for a time sufficient to generate the hydrogen rich gas while maintaining the CO content less than about 5 volume percent.

26. The method of claim 25, wherein the hydrocarbon fuel is natural gas.

27. The method of claim 25, wherein the hydrocarbon fuel is gasoline.

28. The method of claim 25, wherein the hydrocarbon fuel includes alkanes.

29. The method of claim 28, wherein the hydrocarbon fuel also includes aromatics.

30. The method of claim 29, wherein the hydrocarbon fuel includes branched alkanes and alkenes.

31. The method of claim 26, wherein the dehydrogenation portion includes a group VIII metal, and the oxide-ion conducting portion is selected from a ceramic oxide from the group crystallizing in the fluorite structure or  $\text{LaGaO}_3$  and mixtures thereof.

Cancel claim 32.

Cancel claim 33.

Cancel claim 34.

**STATEMENT UNDER ARTICLE 19**

The claims are amended to conform to the claims of corresponding U.S. patent application serial no. 08/867,556 filed June 2, 1997 and application serial no. 09/092,190 filed June 5, 1998, which is a divisional of the prior filed '556 application.

ANY REFERENCES TO FIGURES 1-4 SHALL BE CONSIDERED NON-EXISTENT

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US98/10523

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : Please See Extra Sheet.

US CL : Please See Extra Sheet.

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : Please See Extra Sheet.

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS

search terms: catalyst, ceramic oxide, ceria, zirconia, platinum, palladium, alkanes, hydrocarbons, etc.

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,380,692 A (NAKATSUJI et al) 10 January 1995, col. 1, line 53 to col. 50, line 34.	1-31
X	US 5,597,771 A (HU et al) 28 January 1997, col. 7, line 30 to col. 27, line 25.	1-31



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
*A* document defining the general state of the art which is not considered to be of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
*E* earlier document published on or after the international filing date	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*A* document member of the same patent family
*O* document referring to an oral disclosure, use, exhibition or other means	
*P* document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

04 SEPTEMBER 1998

Date of mailing of the international search report

16 SEP 1998

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# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US98/10523

## Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
  
2. ☐ Claims Nos.:  
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
  
3. ☐ Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

Please See Extra Sheet.

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☒ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:  
1-31

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.  
☐ N protest accompanied the payment of additional search fees.

# INTERNATIONAL SEARCH REPORT

International application No.

PCT/US98/10523

## A. CLASSIFICATION OF SUBJECT MATTER:

IPC (6):

B01J 29/04, 29/06, 21/00, 23/40, 23/58, 23/44, 23/42, 23/02, 23/20, 23/00; C04B 35/48, 35/03, 35/20; H01M 4/86, 8/08;  
G01N 27/26

## A. CLASSIFICATION OF SUBJECT MATTER:

US CL :

502/326, 327, 328, 330, 333, 334, 339, 340, 341, 354, 355, 61, 65, 73, 74  
204/421; 501/103, 126, 152; 429/40, 41, 42, 43, 44, 45, 46

## B. FIELDS SEARCHED

Minimum documentation searched

Classification System: U.S.

502/326, 327, 328, 330, 333, 334, 339, 340, 341, 354, 355, 61, 65, 73, 74  
204/421; 501/103, 126, 152; 429/40, 41, 42, 43, 44, 45, 46